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PROTECTION OF COPPER AGAINST HIGH-TEMPERATURE CORROSION

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The optimum composition of a glass matrix for glass enamel coating on copper is developed. The paper gives the optimum concentrations for Fe_3O_4 , MnO_2 , and Co_2O_3 additives, whose introduction during slip milling increases the adhesion strength of the coating and its heat resistance. A mechanism for the formation of coating on copper is suggested.

An important factor in extending the service life of copper work-coils used in the production of machinery and railway engines is the development of various methods to protect work-coils from scale formation and burning through, and to prevent the possibility of "shorting" a work-coil to the casing of tempered parts at the moment of their contact. The most efficient and expedient method for protecting a work-coil from the specified effect is the use of glass-enamel coating with increased heat resistance. In this context, the most expedient are single-layer glass enamel coatings without a priming layer.

The main factor affecting service qualities of protective glass enamel coating is the strength of its adhesion to metal, which is chiefly determined by the structure and the phase composition of the interface copper-coating layer. The quality and service properties of an enameled article depend on the nature, rate, and completeness of the physicochemical processes that take place inside the coating and in the reaction between the melt and the metal in the course of firing. The nature of these processes varies and is primarily determined by the coating composition and properties, the quality of the metal surface treatment, and the temperature and duration of firing. The phase composition and the microstructure of a coating are formed in firing and determine the physicomachanical, electrical, thermal, and other properties of enameled products.

Some researchers pay special attention to formation of coatings on copper surfaces. However, the available data on this stage of enameling are contradictory, and the essence of the process is not sufficiently studied. In this context, an inquiry into the physicochemical processes occurring during the coating formation in firing is quite important.

It is known [2] that single-layer glass enamel coatings for copper are relatively low-melting and their compositions are usually arranged within the $\text{R}_2\text{O} - \text{PbO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ sys-

tem. The low-melting component in this system is PbO . However, considering the environmental restrictions, the presence of lead-containing compounds in the composition of coatings is extremely undesirable. Therefore, the synthesis of lead-free protective coatings is topical and promising.

For this purpose, we adopted certain concentration limits of the main oxides which amounted to (% hereafter weight content is indicated): 18 – 60 SiO_2 , 5 – 20 B_2O_3 , and 4 – 40 R_2O with weight ratio of alkaline oxides $\text{R}_2\text{O} = 1.3$, $\text{Na}_2\text{O} + 1.0 \text{K}_2\text{O}$. The sum of the other components including Al_2O_3 , CaO , and BaO in respective amounts of 7, 5, and 8% was chosen constant and equal to 20%.

To study the glass-forming capacity of glass matrices, glasses of 18 different compositions were synthesized (Table 1).

TABLE 1

Mix- ture*	Weight content, %				State of material after melting
	SiO_2	B_2O_3	Na_2O	K_2O	
1	48.0	4.0	15.8	12.2	Partly opacified glass
2	48.0	10.4	12.2	9.4	Transparent glass
3	48.0	16.0	9.0	7.0	The same
4	44.0	4.0	18.1	13.9	Partly opacified glass
5	44.0	8.0	15.8	12.2	The same
6	44.0	12.0	13.6	10.4	Transparent glass
7	40.0	16.0	13.6	10.4	The same
8	40.0	8.0	18.1	13.9	Partly opacified glass
9	32.0	16.0	18.1	13.9	The same
10	45.6	11.2	13.1	10.1	Transparent glass
11	36.0	13.6	17.2	13.2	Yellow glass
12	36.0	16.0	15.8	12.2	Transparent glass
13	44.0	4.8	17.5	13.7	The same
14	40.0	10.0	16.9	13.1	The same
15	44.8	13.6	12.2	9.4	The same
16	41.0	11.0	15.8	12.2	Partly opacified glass
17	44.8	11.2	13.6	10.4	Clear glass
18	44.0	10.0	14.7	11.3	Yellow glass

* All mixtures contained 7.0% Al_2O_3 , 5.0% CaO , and 8.0% BaO .

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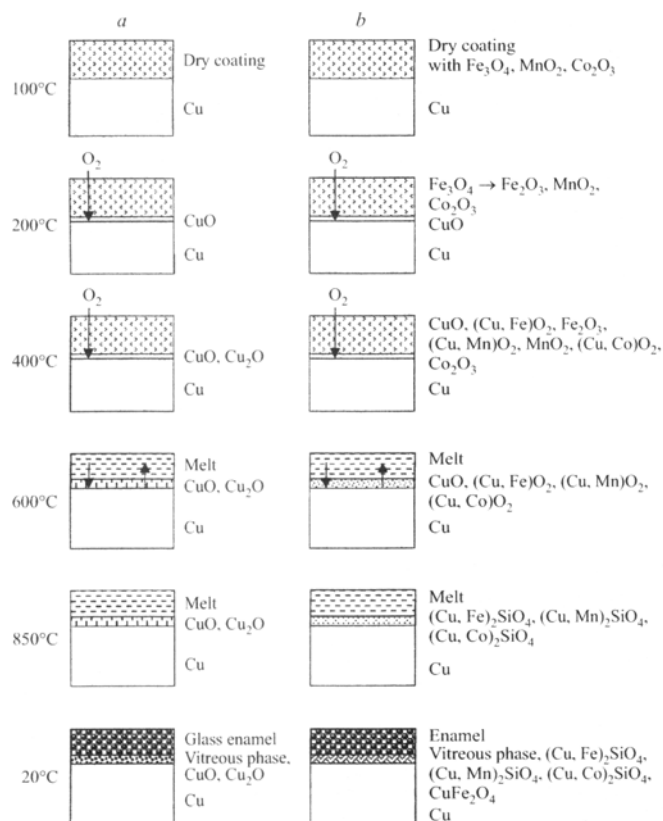


Fig. 1. Scheme of formation of lead-free silicate enamel on copper without additives (a) and with Fe_2O_4 , MnO_2 , and Co_2O_3 additives (b).

TABLE 2

Mixture	Average adhesion index with 7-mm drawing	TCLE, 10^{-7} K^{-1}
1	70	120
2	88	130
3	78	115
4	68	115
5	70	117
6	84	125
7	78	115
8	65	120
9	63	118
10	91	135
11	70	115
12	65	117
13	65	120
14	60	118
15	86	127
16	63	120
17	84	125
18	88	130

The melting temperature of enamel glasses is around 1200°C . Therefore, tests were carried out by melting mixtures in porcelain ladles to obtain glass enamel frits at temperature $1150 - 1200^\circ\text{C}$ with holding for 0.5 h. The content of the ladles after melting was cooled in air, visually in-

spected, and then analyzed with an MBS-1 microscope. The results of the study of glass formation of experimental mixtures indicate that all 18 mixtures form glasses; however, their quality is different. The majority of the glasses are transparent, homogeneous, and have uniform luster (2, 3, 6, 7, 10, 12 – 15). Some of them have yellow shade, others are clear. Glasses 1, 4, 5, 8, 9, and 16 are partly opacified, which, apparently, is the consequence of phase crystallization upon slow cooling in air.

Since the strength of adhesion to metal, as well as coordination between the TCLE of metal ($162 \times \text{K}^{-1}$) and enamel, are especially significant for protective glass enamel coatings, these properties had to be studied in all 18 frit compositions. For this purpose, 18 enamel slips were prepared which had the following composition (%): 100 frit; above 100%: 3.0 clay from Chasov-Yar deposit, 0.1 potassium, 40.0 water.

In firing, transparent clear glass enamel coatings were formed on copper, mostly with a smooth, even surface, without extraneous inclusions, with a small amount of pinpricks. The optimum firing temperature of the enamel coatings was 850°C .

The enamels were tested for their adhesion strength using the gradual drawing method developed at Novocherkassk Polytechnic Institute [3], and the TCLE was determined on a DKV-4 vertical quartz dilatometer. The measurement results (Table 2) show that out of 18 frits, glass matrix 10 had the optimum composition with respect to adhesion strength and the TCLE and was selected for further studies.

The strength of enamel adhesion to metals is greatly influenced by oxides which are adhesion activators introduced in milling slips. They determine the processes occurring during the formation of glass enamel coating on copper and, consequently, the adhesion strength of the copper – enamel composite and its heat resistance.

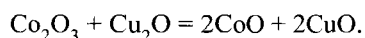
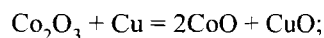
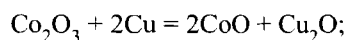
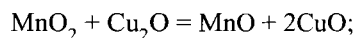
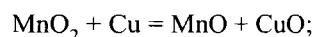
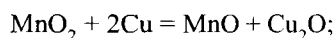
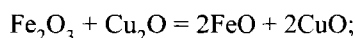
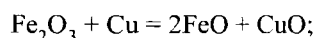
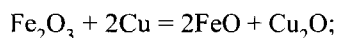
It was found that optimum properties were exhibited by enamels with 0.51 – 1.98% Co_2O_3 , 0 – 4.50% Fe_2O_4 and 3.30 – 9.30% MnO_2 additives. When these additives were introduced into the enamel slip, the maximum values of adhesion strength and heat resistance were 98% and 72 cycles ($20 - 400^\circ\text{C}$), respectively.

In developing a technology for protecting copper coils employing glass enamel coating, it is important to study the process of coating formation in firing. The studies carried out by the authors revealed the following sequence of processes occurring in the formation of glass enamel coatings in firing (Fig. 1).

When enamel is used without Fe_2O_4 , MnO_2 , and Co_2O_3 additives, until the moment of frit particle fusing at 580°C , air oxygen penetrates through the porous layer in the temperature interval of $200 - 375^\circ\text{C}$ and oxidizes copper to CuO . At higher temperatures, Cu_2O is formed in the contact layer between copper and glass enamel due to reduction of CuO to Cu_2O under a deficit of oxygen, and the upper layer is CuO . With further heating, the electric conductivity of the coating

is changed, a melt is formed, and the access of oxygen to the copper substrate is impeded. After the formation of the melt and until the firing of the enamel coating is completed, CuO and Cu₂O of the interface zone are dissolved in the adjacent enamel layer. Moreover, copper is additionally oxidized due to the rupture of bonds between Cu²⁺ and O²⁻ ions in the melt and emergence of a bond between O²⁻ ions and the copper surface atoms. This bond contributes to adhesion of the coating to the copper. Thus, an interface layer is formed between copper and enamel in firing and upon chilling of the coating, which layer consists mostly of a vitreous phase saturated with CuO and Cu₂O which form part of its structural formula and ensure the adhesion strength.

In the case where Fe₂O₃, MnO₂, and Co₂O₃ additives are introduced in milling, the process of formation of a coating on copper is different. The presence of adhesion activators in the contact zone intensifies the chemical activity of the reactant phases and facilitates the following electrochemical reactions:



The emerging FeO, MnO, and CoO react with CuO and form solid solutions (Cu,Fe)O₂, (Cu,Mn)O₂, and (Cu,Co)O₂, which react with silicate melt, in particular with [SiO₄]⁴⁻ anions, and form the respective silicates (Cu,Fe)₂SiO₄, (Cu, Mn)₂SiO₄, (Cu, Co)₂SiO₄, as well as the spinel-type compounds CuFe₂O₄, which is supported by the data of x-ray phase analysis (Fig. 2). The formation of these silicates takes place in the interface layer between copper

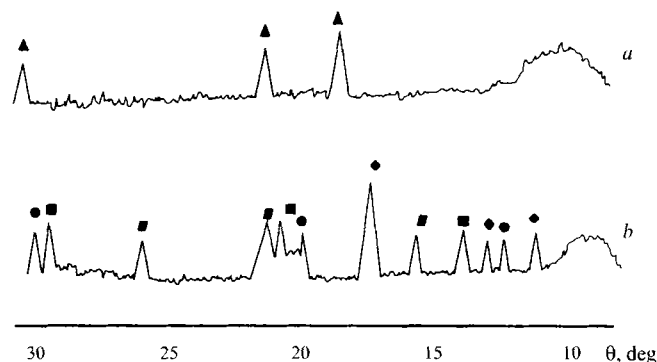


Fig. 2. X-ray patterns of glass enamels on copper without additives (a) and with Fe₃O₄, MnO₂, and Co₂O₃ additives (b): ▲ — CuO; / — CuFe₂O₄; ■ — (Cu, Co)₂SiO₄; ◆ — (Cu, Fe)₂SiO₄; ● — (Cu, Mn)₂SiO₄.

and the vitreous silicate coating. Silicates which have a filamentary (needle-shaped) structure are the reinforcing elements of the interface layer frame structure, which determines the high strength of the composite adhesion.

This is supported by the electron microscope data. The coating with Fe₃O₄, MnO₂, and Co₂O₃ additives, in contrast to the coating without additives, has a clearly expressed transitional layer between the coating and the copper. Moreover, the metal surface is loosened as a consequence of the chemical reactions that take place. Therefore, in the presence of Fe₃O₄, MnO₂, and Co₂O₃ additives, the adhesion strength provided by the oxide interlayer of Cu₂O and CuO related to the glass enamel increases due to the formation of silicates and spinels which intersperse the vitreous phase.

Thus, we have clarified the mechanism of the formation of coating on copper and determined the role of Fe₂O₃, MnO₂, and Co₂O₃ additives, whose introduction in the course of slip milling increases the adhesion strength of the coating and its heat resistance.

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